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PREPARATION AND PROPERTIES OF CUBIC ZRO2 STABILIZED
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PREPARATION AND PROPERTIES OF CUBIC ZrO_2 STABILIZED WITH $Ni(II)$

by

K. E. Smith, R. Kershaw, K. Dwight and A. Mold

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Preparation and Properties of Cubic ZrO_2 Stabilized with Ni(II)

by

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ABSTRACT

Samples of cubic stabilized ZrO_2 have been prepared by the codecomposition of nickel nitrate and zirconyl nitrate at 500°C . A comparison of the stability towards reduction of the bulk NiO and the Ni(II) in the cubic stabilized ZrO_2 demonstrates the influence of the stabilization of cubic ZrO_2 with Ni(II) .

MATERIALS INDEX: Nickel nitrate, Nickel oxide, Zirconyl nitrate, Zirconium oxide.

Introduction

Nickel oxide has been studied on a variety of support materials ~~such as~~ Al_2O_3 (1, 2), ZrO_2 (2), MgO (3), TiO_2 (3), and SiO_2 (4). The Fischer-Tropsch activity of the nickel-zirconia system has been investigated and preparations of the catalyst involving coprecipitation gave a significantly more active catalyst than did preparations involving impregnation (5). Stabilization towards reduction has been observed when certain transition metal ions such as Rh(III) are inserted into the fluorite ZrO_2 structure (6). Recent investigations using the NiO/ZrO_2 system have concluded that NiO does not interact with ZrO_2 , but the materials were prepared by incipient wetness (7).

It was the purpose of this study to investigate the formation of cubic ZrO_2 stabilized with Ni(II) and to relate the structural properties of the catalyst with its observed stability in reducing atmospheres. These properties were then compared to those of catalysts prepared by incipient wetness. Changes in the structure of ZrO_2 and in the temperatures at which reduction of Ni(II) to Ni metal occurred were then related to the relative strengths of the catalyst-support interaction.

Experimental

Samples of cubic ZrO_2 stabilized with Ni(II) were prepared to give compositions ranging between 10 and 30 mole percent calculated as NiO . The desired quantities of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aesar 99.7%, lot 011783) and $\text{ZrO(NO}_3)_2$ (8) were dissolved in distilled water. Ten ml of water were added for each gram of $\text{ZrO(NO}_3)_2$. The molecular weights of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO(NO}_3)_2$ were determined by thermogravimetric analysis and found to be 298 and 245 respectively, compared to the calculated values of 291 and 231. The differences between the experimental and theoretical values are due to the hygroscopic nature of the

nickel nitrate and adsorbed water on the zirconyl nitrate. The solutions were then dried at 150°C for 24 hours, ground in an agate mortar and heated in air at 500°C for 34 hours. Bulk $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the double salt of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2$ were dissolved in distilled water and dried at 150°C for 24 hours. The material resulting from this drying was decomposed in a thermogravimetric balance under a predried flowing oxygen atmosphere with a flow rate of 30 ml/minute. The samples were heated to 700°C at a rate of 100°C/hour.

Samples prepared by incipient wetness were obtained by drying an aqueous slurry of tetragonal ZrO_2 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 150°C for 24 hours. The resulting material was then ground in an agate mortar and decomposed in air at 500°C for 34 hours. This temperature was chosen to facilitate the comparison between these samples and those prepared by codecomposition.

The temperature programmed reductions of bulk NiO as well as samples containing calculated values of 10, 16 and 30 mole percent of NiO were carried out in a thermogravimetric balance. These reductions were also studied on a thermogravimagnetic balance (9). The resulting data gives two kinds of information: first, the normal thermogravimetric data is obtained (loss of weight as a function of temperature) and second, the oscillating weight changes are obtained which reflect the field on and field off environment of the sample. For example, as antiferromagnetic NiO is reduced to ferromagnetic Ni metal, the oscillating signal from the magnet increases until the Curie temperature is reached and then decreases again.

Characterization of Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405\text{\AA}$). The diffraction patterns were taken in the range of $12^\circ < 2\theta < 72^\circ$ with a scan rate of $1^\circ 2\theta/\text{minute}$ and a chart speed of 30 inches/minute.

The temperature programmed reductions were performed in a Cahn System 113 thermal balance. The heating rate was 30°C/hour up to 950°C in an atmosphere of a predried 85%Ar/15%H₂ mixture.

The thermogravimagnetic studies were performed in a balance which was designed and built in our laboratory (9). This balance incorporates a Cahn RG electrobalance and has a pivoted permanent magnet that sweeps through the area surrounding the sample bucket at a rate of one revolution per minute.

The magnetic measurements were performed on the Faraday balanced described by Morris and Wold (10). The susceptibility was measured from 77 K to room temperature and was corrected for the theoretical core diamagnetism.

Results and Discussion

Samples of Ni(II)/ ZrO_2 were prepared by double decomposition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2$. The temperature programmed decompositions of both bulk nickel nitrate and bulk zirconyl nitrate, as well as the double salt of nickel and zirconyl nitrates, were carried out in order to compare their

decomposition temperatures. Pure nickel nitrate decomposes to the oxide at $320 \pm 15^\circ\text{C}$. This is in agreement with results reported by Weigel et al. (11). The final product was gray and gave an x-ray pattern that corresponded to cubic NiO. Decomposition of zirconyl nitrate at 500°C in air for 4 hours showed predominantly tetragonal ZrO_2 with a small amount of the monoclinic phase. With prolonged heating (34 hours) of the sample, the observed amount of the monoclinic phase continued to increase. With a rate of heating of $100^\circ\text{C}/\text{hour}$, the decomposition of the corresponding double salt was observed to be essentially complete by 500°C , and therefore this temperature was chosen for the decomposition of the double salts.

A sample of the double salt was prepared such that the resulting decomposition would give 10 atomic percent Ni(II)/ZrO_2 . X-ray patterns of the products taken after 4 hours and after 34 hours at 500°C (in air) were identical and showed cubic ZrO_2 . The lack of additional decomposition during the longer heating period suggests that complete decomposition was obtained. Fig. 1 shows

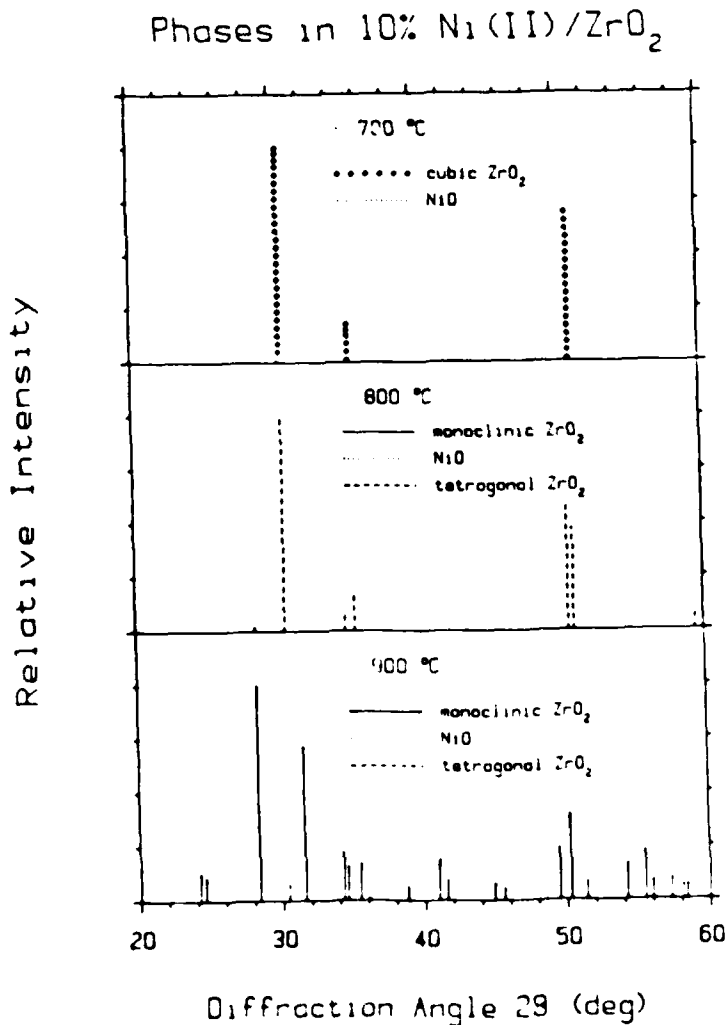


Fig. 1. Phase analysis as a function of temperature for 10 atomic percent Ni(II) in ZrO_2

that the stabilized cubic phase of ZrO_2 containing 10 atomic percent Ni(II) persists below 800°C . At 800°C the tetragonal phase predominates. By 900°C the phase is essentially all monoclinic and the (012) and (101) peaks of NiO are now much more intense. This indicates that the Ni(II) is no longer in solid solution with ZrO_2 .

When the introduction of Ni(II) was attempted through incipient wetness techniques, no stabilization of the cubic ZrO_2 was observed. For such samples prepared at 500°C , both the tetragonal and monoclinic phases were observed although the tetragonal peaks at 50.2° were not clearly resolved (Fig. 2). The NiO peaks (012 and 101) were clearly evident. These results suggest that codecomposition of the nitrates is the method of choice to obtain a solid solution of Ni(II) in ZrO_2 .

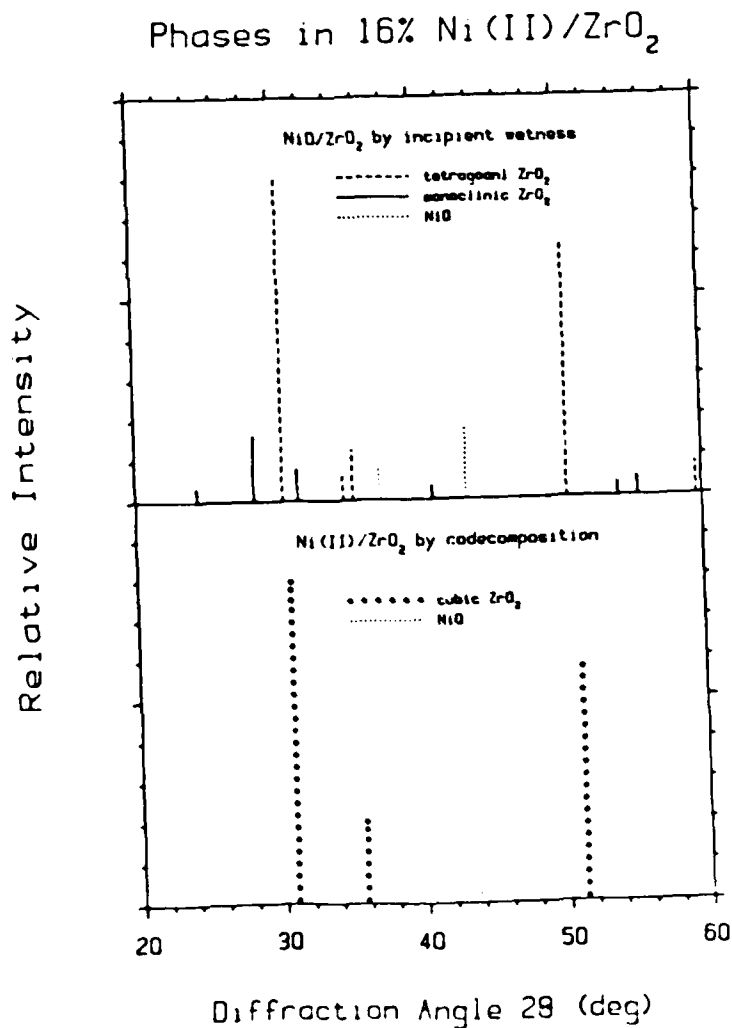


Fig. 2. Phase analysis of samples of 16 atomic percent NiO/ZrO_2 (incipient wetness), and $\text{Ni(II)}/\text{ZrO}_2$ (codecomposition) prepared at 500°C .

From x-ray analysis it was determined that products of the cubic stabilized ZrO_2 prepared at 500°C were single phase up to a concentration of approximately 16 atomic percent Ni(II) . Samples containing more than 16 atomic percent Ni(II) showed the presence of bulk NiO as indicated by x-ray analysis. The thermogravimagnetic data for the 16 atomic percent sample in a reducing atmosphere shows that the signal from the magnet begins to increase at 310°C and concurrently the weight begins to decrease. This demonstrates that the decrease in weight corresponds to the appearance of Ni particles. Therefore, the reduction of Ni(II) to Ni metal may be followed either as a function of weight loss or by growth of the signal resulting from the formation of a magnetic phase (Ni).

Under the same conditions, a 10 atomic percent Ni(II) sample shows no magnetic signal or weight loss at 310°C . In fact, no Ni metal was detected as the temperature was raised up to the Curie temperature (358°C). Therefore, the maximum amount of Ni(II) that can form solid solution with ZrO_2 is between 10 and 16 atomic percent Ni(II) . It can be seen in Fig. 3 that, for the sample containing 10 atomic percent Ni(II) , only one reduction step is observed, which is due to the reduction of Ni(II) in the ZrO_2 . For samples with 16 atomic percent Ni(II) and higher, two reductions are observed. The reduction at the lower temperature is due to bulk NiO ; that at the higher temperature is due to reduction of Ni(II) present in the ZrO_2 .

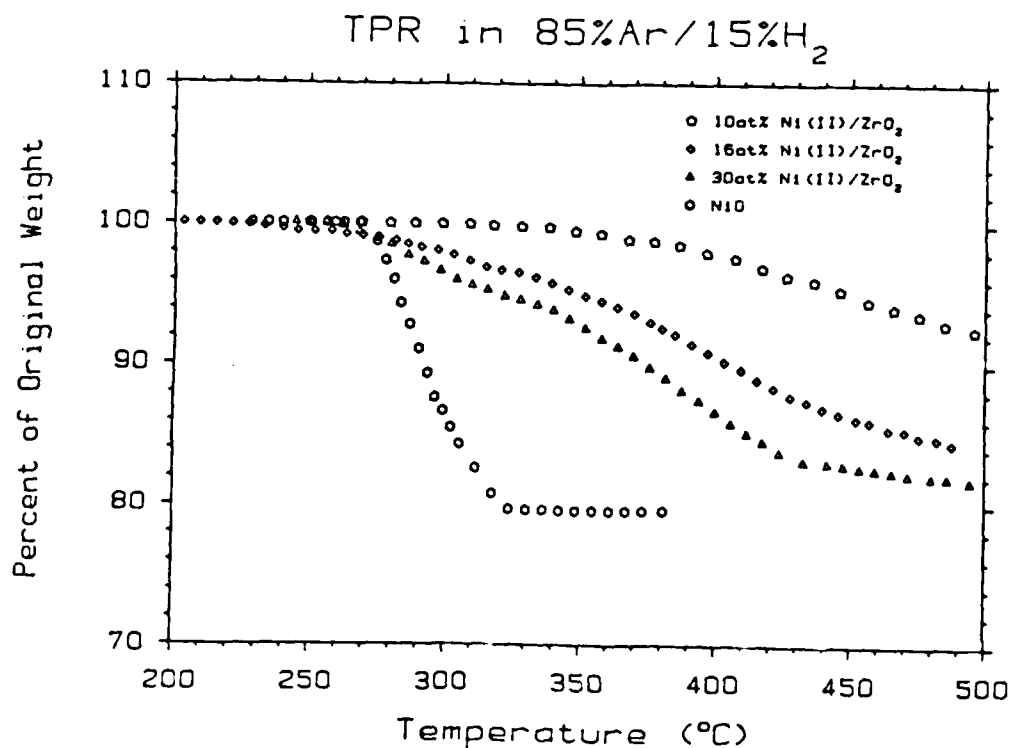


Fig. 3. Temperature programmed reduction in $85\%\text{Ar}/15\%\text{H}_2$ of Ni(II)/ZrO_2 and NiO

Bulk NiO prepared from the nitrate and decomposed at 500°C shows antiferromagnetic behavior. However, the temperature dependence of the magnetic susceptibility of the Ni(II) in solid solution with ZrO₂ shows paramagnetic behavior with weak antiferromagnetic interactions and a moment of 3.1 BM. Interpretation of the deviation from the spin-only moment of 2.8BM would be dependent on the coordination of the Ni(II) in the fluorite structure. Preliminary results suggest that it is possible to have a first row transition metal in 8-fold coordination (Zr sites or in the equivalent site found in the central cavity of the fluorite cubic cell).

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